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THIS IS UNEVALUATED INFORMATION FOR THE RESEARCH
USE OF TRAINED INTELLIGENCE ANALYSTSSOURCE IDENTIFICATION Investiya Akademii Nauk SSSR, Otdeleniye Khimicheskikh Nauk, No 2, 1948. (FDB Per Abs 63T5 -- Translation specifically requested.)KINETICS OF EXOTHERMIC CATALYTIC REACTIONS IN A STREAMIV. STATIONARY AND NONSTATIONARY THERMAL CYCLES OF
OXIDATION OF ISOOCTANE ON A COPPER-CHROMIUM CATALYSTL. Ya. Margolis and O. M. Toles
Institute of Physical Chemistry
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Submitted 8 April 1947[Tables and figures referred to herein are appended.]

In the first and second parts of the work [1, 2] a detailed theoretical analysis was conducted of the possible thermal cycles of exothermic catalytic reactions in a stream. In the third part [3, 4] was studied experimentally the kinetics of the catalytic oxidation of isooctane on various catalysts under isothermal conditions in the kinetic zone. The results obtained permit one to predict the conditions and laws of the transition of the process from the zone of "quiet reaction" to the zone of "heterogeneous combustion," and to verify these predictions experimentally.

Thermal Characteristics of the Apparatus

The apparatus on which the investigation was conducted has been described in detail in the previous part of the work [3, 4]. In studying the thermal cycles of oxidation of isooctane, a reaction tube was filled with a copper-chromium catalyst deposited on asbestos.

Losses of heat in the reaction vessel are determined, on the one hand by the outward discharge of heat through the walls of the vessel, and on the other hand, by the removal of heat with a current of gas from the vessel. The quantity of heat removed by the current of gas per unit of time is equal to

$$(Q_2 = c_p U S (T_v - T_0)) \quad (1)$$

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where op is the specific heat of the gas at constant pressure;
 US is the volume speed of current;
 S is the area of the cross section of the reaction vessel;
 T_0 and T_v are the temperature of gas on entering and leaving the vessel.

The special experiments made showed that under these conditions the heat carried off by the gas current constitutes only an insignificant portion of the full heat loss. The results of this series of experiments are given in Table 1, which shows that the losses of heat with the gas current constitute usually only 3-9 percent of the total heat balance. Thus the basic heat loss is determined by the emission of heat through the walls of the reaction vessel.

The speed of heat emission can be characterized by the so-called "time of relaxation" or "characteristic time" t_c .

During a stationary cycle, when the incoming heat from the reaction is balanced by the heat emission outwards, a definite initial heating of the reaction vessel ΔT is established, which is proportional to the speed of heat emission during the reaction Q and:

$$\frac{Q}{C_3} = \frac{\Delta T}{t_c}, \quad (2)$$

where C_3 is the specific heat of the reactor.

In a nonstationary cycle, when the external source of heat is cut off ($Q=0$), the initial heating drops with time according to the exponential law:

$$\Delta T = \Delta T_0 e^{-t/t_c} \quad (3)$$

Expressions (2) and (3) permit one to determine magnitude t_c on the basis of the experimental study of a stationary or nonstationary thermal cycle. During heat emission through the walls, the characteristic time t_c , for a cylinder of radius r , with the specific heat of a volume unit of the substance of this cylinder (in this case of the charge) c_3 must be equal to:

$$t_c = \frac{r^2 c_3}{\alpha c}, \quad (4)$$

where αc is the coefficient of heat transmission outward through the walls. For circular tubes of small diameters this coefficient of heat transmission is usually of the order of $10 \frac{\text{Watt cm}^2}{\text{deg. cm}^2} = 5000 \frac{\text{cal}}{\text{deg. sec. cm}^2}$

Consequently, when $r = 1.1 \text{ cm}$ and $C_3 = 0.45 \frac{\text{cal}}{\text{deg. cm}^3}$ (asbestos), the expected magnitude t_c must be of the order of 5 minutes. Under these conditions, when the heating spiral on the reaction vessel was not covered from the outside with a heat insulator, it was natural to expect somewhat greater values of α , and therefore a shorter characteristic time t_c .

In the experimental determination of magnitude t_c , we used Formula (3), converted to logarithmic coordinates:

$$\log(\Delta T) = \log(\Delta T_0) - \frac{1}{2.3} \frac{t}{t_c}. \quad (5)$$

From three thermocouples placed at various depths in the charge, the curves of cooling for the middle and lower thermocouples practically coincided with one another; but the readings of the upper thermocouple, which was submerged in the charge to a depth of 0.5 cm, lagged behind by several degrees (Figure 1). In Figure 2 the curves of cooling are given in logarithmic coordinates at various speeds of the gas stream passing through the reaction vessel. As may be seen from the graph, the logarithmic relation-

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ship (5) is fulfilled rather well in the interval above 100° , and is practically independent of the speed of the stream. With the increase of temperature from 300 to 600° , the magnitude t_c decreases from 2.5 to 0.5 minutes (Figure 3). The data on stationary initial heating of the reaction vessel, in accordance with formula (2), lead approximately to the same values for $t_c \approx 2$ minutes.

Stationary Thermal Cycles During Oxidation of Isocotane on Catalysts of Varying Activity

As the previous work [3] revealed, the speed of decrease of the isocotane concentration in a stream c with time is determined by the equation:

$$-\frac{dc}{dt} = K(T)c^2, \quad (6)$$

where $K(T) = K_0 e^{-E/RT}$ is the constant of speed of the reaction, which is proportional to the concentration of the contact on the carrier. The speed of increase in temperature of the reaction vessel due to the heat liberated during the reaction, with a calculation of the burning out and drop of the concentration of the reacting substance along the stream, is equal to:

$$\left(\frac{dT}{dt}\right)^+ = \frac{\gamma}{c_0} K(T) c_0^2 \left\{1 - \frac{T - T_0}{T_m - T_0}\right\} \quad (7)$$

(see Formula 24 of the previous work). Here γ is the thermal effect of the reaction; T_0 is the effective temperature of heating; $T_m - T_0$ is the maximum initial heating during full combustion.

The speed of fall of temperature under the same conditions as a result of heat emission is determined by the expression:

$$\left(\frac{dT}{dt}\right)^- = \frac{T - T_0}{t_c} \quad (8)$$

Figure 4 shows the curves of the speed of initial heating (solid lines) and the speed of cooling (dotted lines) under various conditions for the oxidation of isocotane on a 10 percent copper-chromium catalyst, calculated according to equations (7) and (8). The curves (8) are not straight, inasmuch as the relation of t_c to the temperature must be taken into account (Figure 3). These curves are naturally very sharply distinguished from one another at various values of the temperature of heating of the reaction vessel.

The curves of the speed of initial heating (7) at a given initial concentration of isocotane c_0 in the stream are also related to T_0 . However, inasmuch as this relationship, which determines the magnitude of the correction factor in burning out $\left\{1 - \frac{T - T_0}{T_m - T_0}\right\}$, is comparatively slight, these curves are given only for $T_0 = 400^\circ$, so as not to encumber the diagram.

As may be seen from Figure 4, when $c_0 = 1.4$ percent by volume, the intersection of curves 8, corresponding to various T_0 from 12 to $400^\circ C$, with curve 7 occurs at temperatures T that are very close to T_0 ; that is, the reaction proceeds with little initial heating in the kinetic zone.

For a somewhat higher initial concentration of the fuel, $c = 1.7$ percent, these correlations are observed only below $T_0 = 400^\circ$. At a temperature of heating $T_0 = 400^\circ$, curves 7 and 8 practically touch for this case; consequently, with a slight overheating, there must ensue a transition of the reaction to the diffusion zone, a sharp rise in temperature, and the concentration of the reaction in a narrow layer in the vicinity of the entrance section of the

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reaction vessel 4. Actually with $T_0 = 400^\circ$ the experiment shows that when $c_0 = 1.7$ percent the reaction goes over to the zone of "heterogeneous combustion"; in order to retain the process in the zone of "quiet reaction" at this value of T_0 , it is necessary to lower the initial concentration of the fuel c_0 .

In Figure 5 similar curves are given for a 30 percent (solid lines) and a 67 percent (double dotted lines) copper-chromium catalyst on asbestos. As may be seen from this figure, when $c_0 = 1.7$ percent for a 30 percent contact, the transition of the reaction to the zone of heterogeneous combustion occurs at $T_0 = 300^\circ$, and for a 67 percent contact, at an even lower temperature. Actually, at a 67 percent contact when $c_0 = 1.7$ percent the kinetics of the catalytic oxidation of isocotane were not successfully measured when $T_0 < 250^\circ$ the speed of the reaction in the kinetic zone was so slight that it appeared impossible to measure it. When $T_0 > 250^\circ$, however the reaction immediately went over to the diffusion zone, and heterogeneous combustion developed in a narrow layer near the entrance to the reaction vessel. Therefore, in order to study the kinetics of the process in the zone of temperatures from 300 to 600°, we had to decrease the concentration of isocotane in the stream and the concentration of the catalyst on the carrier.

Under these conditions was successfully effected a stationary cycle of reaction with initial heatings calculated from the condition of the equality of speeds of initial heating and cooling:

$$\frac{T - T_0}{t_c} = K(T) c_0^2 \left(1 - \frac{T - T_0}{T_m - T_0} \right) \quad (9)$$

As a rule, these initial heatings $T - T_0$ over the temperature of external heating were not great, but under separate conditions at high temperatures they reached ~100°. In Table 2 the results of a series of experiments are given in which we determined experimentally the magnitude of this initial heating. For this, temperature T of a stationary reaction was determined according to the indications of a thermocouple; then the delivery of isocotane was cut off, and the temperature of heating T_0 was measured under the same conditions of the experiment, but in the absence of a reaction. In the last column of the table the values of initial heating $T - T_0$, calculated theoretically for the same experiments according to equation (9), are given for comparison.

As may be seen from Table 2, the agreement between the theoretical and experimental values of initial heating $T - T_0$ is completely satisfactory.

Nonstationary Cycle of "Extinction"

By bringing the reaction to heterogeneous combustion and shutting off or weakening the external heating (that is, having greatly decreased the effective temperature of heating T_0), one enters the zone of temperatures in which:

$$\left(\frac{dT}{dt} \right)^- > \left(\frac{dT}{dt} \right)^+$$

The temperature of the reaction vessel will begin to fall, and the reaction will be "extinguished," that is, it will go over to the kinetic zone with comparatively small initial heatings and speeds of reaction. The speed of fall of temperature for this cycle of "extinction" of the reaction must be determined by the correlation:

$$\frac{dT}{dt} = \left(\frac{dT}{dt} \right)^+ - \left(\frac{dT}{dt} \right)^- < 0. \quad (10)$$

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A series of experiments were conducted in which was measured experimentally the curves of fall of temperature with time during a similar extinction of the reaction for copper-chromium contacts of varying activity at various temperatures of heating of the reaction vessel T_0 . The data on these experiments is given in Figure 6 and Table 3.

In this table for comparison the theoretical values of the absolute speed of cooling $\left(\frac{dT}{dt}\right)$, calculated according to formula (10) were contrasted.

As is seen, the agreement between the theoretical and experimental values of the magnitude of $\left(\frac{dT}{dt}\right)$ is completely satisfactory.

As was indicated in one of our previous works [2], the speed of fall of temperature in a nonstationary cycle of extinction, with other conditions equal, is determined by the activity of the contact K , and decreases with the increase of the latter approximately according to the linear law:

$$\frac{dT}{dt} \approx A - BK. \quad (11)$$

As may be seen from Table 3, this correlation is qualitatively justified experimentally in a thoroughly satisfactory manner and the magnitude of $\left(\frac{dT}{dt}\right)$ may characterize the comparative activity of various catalysts.

Conclusions

1. On the basis of the theoretical analysis of the thermal cycles of exothermic catalytic reactions in a stream [1,2] and the experimental study of the kinetics of the catalytic oxidation of isooctane on a copper-chromium catalyst [3,4], the conditions of the transition of this reaction from a cycle of "quiet oxidation" to a cycle of "heterogeneous combustion" were predicted.
2. The transition of this reaction from one thermal cycle to another was experimentally achieved at the predicted theoretical values of the initial concentration of isooctane in a stream - c_0 , of the effective temperature of heating of the reaction vessel T_0 , and of the activity of the catalyst, which is proportional to the concentration of the latter on an asbestos carrier.
3. With a cycle of "quiet oxidation" in a number of experiments, the stationary self-heatings of the reaction were measured and the magnitudes of these seemed to coincide very satisfactorily with the values calculated theoretically according to equation (9).
4. In a nonstationary cycle of "extinction" of the reaction, the speeds of fall of temperature with time $\left(\frac{dT}{dt}\right)$ were measured and were in satisfactory agreement with the magnitudes calculated theoretically according to equation (10). Moreover, the idea, previously expressed [2], concerning the possibility of the comparative estimate of the activity of various catalysts according to the magnitude $\left(\frac{dT}{dt}\right)$, measured under identical conditions, was confirmed.
5. Both types of thermal cycles analyzed and produced under laboratory conditions may take place in the catalytic industry for strongly exothermic reactions. In these cases it is very important from a practical standpoint to be able to produce the necessary type of thermal cycle, and to know the limits of stable existence of this cycle, established in the given series of works.

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It is also necessary to emphasize the primary necessity of avoiding the development of a cycle of heterogeneous combustion in the study of the temperature relationship of the activity of catalysts being tested in the laboratory, inasmuch as it is impossible, with this cycle, to preserve isothermal conditions of work of the whole catalyst understudy.

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[Appended figures follow.]

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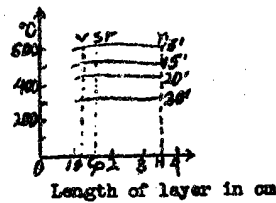


Figure 1. Equalization of temperature according to the layer of contact: v is the upper thermocouple; m is the middle thermocouple; n is the lower thermocouple.

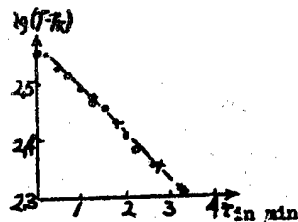


Figure 2. Kinetics of cooling of contact at various speeds of flow of gas (speed of flow in l/hour: 16 l/h; 27 l/h; 44 l/h).

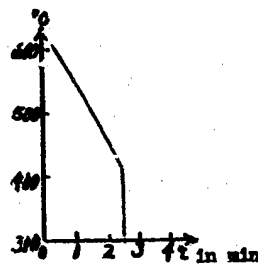


Figure 3. Relation of the characteristic magnitude t_0 to the temperature.

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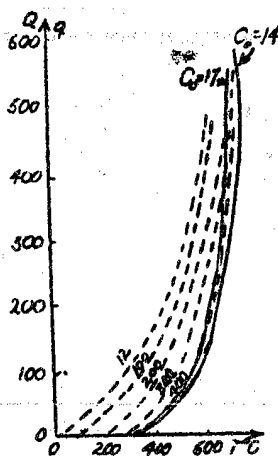


Figure 4. Relation of the speed of heat income and heat emission to temperature for a 10 percent copper-chromium catalyst.

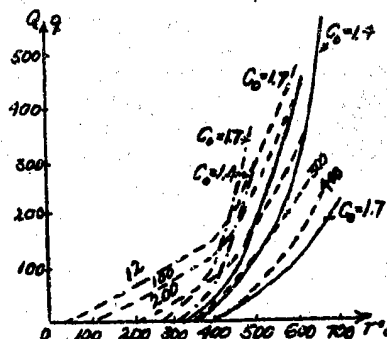


Figure 5. Relation of the speed of heat income and heat emission to temperature for a 30 and 67 percent copper-chromium catalyst.

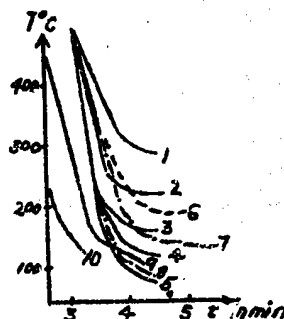


Figure 6. Relation of temperature to time for a 10, 30, and 67 percent copper-chromium catalyst at varying values: 1-10 percent contact $T_0 = 300^\circ$; 2-10 percent contact $T_0 = 250^\circ$; 3-10 percent contact $T_0 = 150^\circ$; 4-10 percent contact $T_0 = 100^\circ$; 5-10 percent contact $T_0 = 12^\circ$; 6-30 percent contact $T_0 = 200^\circ$; 7-30 percent contact $T_0 = 150^\circ$; 8-30 percent contact $T_0 = 12^\circ$; 9-67 percent contact $T_0 = 12^\circ$.

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Table 1. Removal of Heat by Gas Current at Various Temperatures

No of Experiment	Temperature (in °C)	Initial Heating $\Delta T - T_0 - T_0$	Amount of heat carried off by gas in cal/g	Heat income from reaction in cal/g	Percent of heat carried off by current	Note
66	340	30	6.42	74.9	9	US-40 1/hour
67	340	36	7.22	93.5	8.4	
73	345	31	7.85	104.1	8.2	
68	395	80	14.7	209.5	7.6	
69	426	110	20.2	346.6	6.4	
70	460	135	25.6	523	5.2	

Table 2. Initial Heating of the Reaction During Stationary Cycle of Reaction in the Kinetic Zone

No of Experiment	% volume (C ₀ in %)	Concentration of catalyst by weight of the carrier (in %)	Temperature (in °C)	Experimental initial heating (T - T ₀) (in °C)	Theoretical initial heating (T - T ₀) (in °C)
124	1.36	30	300	5	6
125	1.77	30	300	10	8
135	1.40	30	400	40	45
185	1.26	10	500	100	120
191	1.26	10	450	75	75
194	1.36	40	350	25	30
197	1.26	40	500	70	
199	1.22	40	300	20	20

Table 3. Speeds of Measurement of Temperature with Time in a Stationary Cycle of Extinction of the Reaction (C₀ - 1.7 percent by volume)

Speed of drop in temperature $\left(\frac{dT}{dt}\right)$ in degrees per minute with a concentration of contact on the carrier							
in °C	T ₀ in °C	10%		30%		67%	
		Experimental	Theoretical	Experimental	Theoretical	Experimental	Theoretical
12	600	-	320	-	-	-	-
	500	-	218	-	108	-	-
	400	140	143	85	105	45	38
	300	107	106	85	105	-	-
100	600	-	230	-	-	-	-
	500	-	170	-	50	-	-
	400	100	105	60	75	45	50
	300	76	80	60	75	90	95
200	600	-	148	-	-	-	-
	500	-	116	-	-	-	-
	400	60	64	42	37	-	-
	300	30	40	30	37	-	-
300	600	-	90	-	-	-	-
	500	-	56	-	-	-	-
	400	-	23	-	-	-	-

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